Supplementary Information for:

Towards lignin valorisation: Comparing homogeneous catalysts for the aerobic oxidation and depolymerisation of organosolv lignin

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temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

S21 **Figure S19**. q-HSQC NMR spectra (500 MHz; DMSO-d_6) of organosolv lignin for a) control experiment (no catalyst **2**) and b) catalytic oxidation using 10 wt. % **2** and 10 wt. % Et_3N. For all runs: solvent: *n*-butyl acetate; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

S22 **Figure S20.** q-HSQC NMR spectra (500 MHz; DMSO-d_6) of organosolv lignin for a) control experiment (no catalyst, TEMPO or base) and b) catalytic oxidation with 10 wt. % CuOTf, 10 wt. % TEMPO and 100 wt. % 2,6-lutidine. For all runs: solvent = DMF; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

S23 **Figure S21.** q-HSQC NMR spectrum (500 MHz; DMSO-d_6) for the reaction of organosolv lignin using with 10 wt. % **2** in the absence of base. For all runs: solvent = 8:1 (v/v) EtOAc/THF; temperature = 80 °C; atmospheric pressure of air; reaction time = 24 h.

S23 **Figure S22.** q-HSQC NMR spectrum (500 MHz; DMSO-d_6) for the catalytic oxidation of organosolv lignin using 10 wt. % **2**, 10 wt. % Et_3N. For all runs: solvent = EtOAc; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 4 h.

S24 **Figure S23.** q-HSQC NMR spectrum (500 MHz; DMSO-d_6) of the reaction of organosolv lignin using catalyst **3**; 10 wt. % **3**. For all runs: solvent = 8:1 (v/v) EtOAc/THF; temperature = 80 °C; sealed vial under atmospheric pressure of air; reaction time = 24 h.

S25 **Figure S24**. q-HSQC NMR spectrum (500 MHz; DMSO-d_6) of the reaction of organosolv lignin for a) control experiment (no 4-acetamido-TEMPO) and b) 5 wt. % 4-acetamido-TEMPO, 10 wt. % HNO_3 (70%), 10 wt. % HCl (37%). For all runs: solvent = 19:1 (v/v) CH_3CN/H_2O; temperature = 65 °C; pressure of synthetic air = 8.2 atm; reaction time = 24 h.

S26 **Figure S25.** q-HSQC NMR spectrum (500 MHz; DMSO-d_6) of the reaction of organosolv lignin for a) control experiment (no catalyst **6**) and b) using 10 wt. % **6** and 100 wt. % pyridine. For all runs: solvent = 1:1 (v/v) MeOH/DMSO; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

S27 **Figure S26.** q-HSQC NMR spectrum (500 MHz; DMSO-d_6) of the reaction of organosolv lignin for 10 wt. % **7**. For all runs: solvent = EtOAc; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

S28 **Figure S27.** q-HSQC NMR spectrum (500 MHz; DMSO-d_6) of the reaction of organosolv lignin using the Chornet method (135 wt. % NaOH, 5 wt. % $CuSO_4$ and 0.5 wt. % $FeCl_3$). For all runs: solvent = THF; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

S29 **Figure S28**. q-HSQC NMR spectrum (500 MHz; DMSO-d_6) of the catalytic oxidation of organosolv lignin using 10 wt. % **2**, 10 wt. % Et_3N. For all runs: solvent = DMSO; temperature = 100 ^oC; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

S30 **Figure S29**. ^1H NMR spectrum (500 MHz; DMSO-d_6) of organosolv lignin.

S31 **Figure S30.** ^1H NMR spectrum (500 MHz; DMSO-d_6) of the catalytic oxidation of organosolv lignin using 10 wt. % **2** and 10 wt. % Et_3N. For all runs: solvent = EtOAc; temperature = 100 ^oC; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

S32 **Figure S31.** Quantitative $^{31}P\{^1H\}$ NMR spectra (121 MHz, line broadening 2.5 Hz) of phosphite esters derived from a) organosolv lignin, b) control experiment (base with no catalyst) and c) residue after the catalytic lignin oxidation using 10 wt. % **2** and 10 wt. % Et_3N. For all runs: solvent = EtOAc; temperature = 100 ^oC; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

Experimental details

General Considerations

ACS-grade solvents tetrahydrofuran (THF), *n*-butyl acetate, ethyl acetate (EtOAc), acetonitrile (CH_3CN), dichloromethane (DCM) and dimethyl formamide (DMF) were purchased from Fisher Scientific. THF HPLC grade Chromasolv™, CuOTf (OTf = trifluoromethanesulfonate), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 4-Acetamido-2,2,6,6-tetramethylpiperidine-1-oxyl (4-acetamido-TEMPO), (*R,R*)-(−)-*N,N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP), 2,6-lutidine, trimethylamine (Et_3N) and diisopropylamine (DIPA) were purchased from Sigma Aldrich or Alfa Aesar. Synthetic air (8% oxygen in argon) was purchased from Linde Canada. DCM and CH_3CN were dried refluxing over CaH_2 for 18 h, distilling at reduced pressure followed by filtration with a plug of activated alumina. The dry solvents were stored under activated molecular sieves (4Å). DMSO-d_6, chroloform-*d* ($CDCl_3$) and acetonitrile-d_3 (CD_3CN) were purchased from Cambridge Isotopes Laboratories, Inc. $CDCl_3$ and CD_3CN were dried refluxing over CaH_2 and distilling at reduced pressure. DMSO-d_6 was dried over activated molecular sieves (4Å). IR spectra were obtained on a Thermo Nicolet NEXUS 670 FTIR spectrometer. Elemental Analysis was performed at the Laboratoire d'Analyse Élémentaire de l'Université de Montréal. Gel permeation chromatography (GPC) analyses were carried out in an Agilent HPLC-GPC equipped with a DAD detector (254.4 nm target wavelength) using 1 mL/min THF at 40 ^oC with a guard column and two Waters columns HR-2 and HR-4 connected in series. The analyses were run in duplicate. The instrument was calibrated using polystyrene standard (109,000-162 Da). The single pressure experiments were carried out using a 50 mL Fike™ pressure reactor (Fike Corporation). Screening experiments were performed using the Freeslate high-throughput facilities in the Centre for Catalysis Research and Innovation (CCRI) at the University of Ottawa. The pressure reactor consists of 4 mL borosilicate glass vials and borosilicate glass beads placed in aluminum 24-well plates, fitted with a Teflon™ gasket and Goretex™ gasket and a cover with one-way check valves (common headspace down the rows). The plates were then encased in high-pressure blocks, placed on a 4-position heated orbital shaker system, pressurized manually with synthetic air, and agitated at 400 rpm. Vanadium complexes **1**,[1] **2**,[2] **3**[3] and **6**[4] were prepared according to the published methods.

Synthesis of H_2BPAMP ligand

H2BPAMP was synthetized following the publish procedure.[5] A solution of 2,4-di-*tert*-butylphenol (5 g, 24.23 mmol) and 2-(aminomethyl)pyridine (1.80 mL, 23.94 mmol) in methanol was heated to reflux for 18 h. The flask was cooled down to -5 ^{o}C for 8 h. The yellow viscous solid was triturated in cold methanol for where a white solid appeared (2.3 g, 30% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.56 (s, 2H, Ar-O*H*), 8.70 (d, 1H, *J* = 4.5 Hz, pyr), 7.70 (1H, *J* = 7.6, 1.0 Hz, pyr), 7.29 (t, 1H, *J* = 6.0 Hz, pyr), 7.24 (d, 2H, *J* = 2.3 Hz, Ar-*H*), 7.14 (d, 1H, *J* = 7.6 Hz, pyr), 6.94 (d, 2H, *J* = 2.3 Hz, Ar-*H*), 3.86 (ov br, 2H, CH_2), 3.82 (ov br, 2H, CH_2), 1.41 (s, 18H, ^{t}Bu), 1.30 (s, 18H, ^{t}Bu); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 154.0, 148.3, 140.6, 137.4, 136.5, 125.3, 123.6, 122.6, 121.4, 56.9, 55.5, 35.2, 34.3, 31.8, 29.8.

Preparation of Organosolv Lignin

Organosolv lignin (extracted with 1:1 ethanol/water from mixed hardwoods - aspen, maple and birch) was provided by Lignol Energy Corporation. Before use, the organosolv lignin was heated at 150 ^{o}C for 4 h under reduced pressure (*ca.* 10 mTorr) to remove volatiles; the black uniform residue was used without further purification in all the experiments. The relative amount of major structural units in the oxygenated aliphatic region in organosolv lignin was determined by integrating the H_α/C_α NMR correlation: 0.67 (β-O-4 **A**), 0.22 (β-5 **B**), 1.0 (β-β **C**) and 0.45 (dibenzodioxocin **D**) (See Figure S11). For the aromatic region, syringyl (**S2/6**), guaicacyl (**G**), oxidized syringyl and guaiacyl (**S''**, **S'**, and **G'**) and, *p*-hydroxyphenyl (**H2/6**) units were detected. The relative ratios of (**S'**+**S''**):S and **G'**:**G** were 0.08 and 0.02, respectively. The ^{31}P NMR spectrum of phosphite esters derived from organosolv lignin showed 15.6 mmol of hydroxyl units per gram of lignin distributed as substituted guaiacyl (**C_5**, 8.0 mmol g^{-1}), *p*-hydroxyphenyl (**H**, 0.6 mmol g^{-1}), guaiacyl (**G**, 2.7 mmol g^{-1}), aliphatic (**AH**, 3.3 mmol g^{-1}) and carboxylic (**CH**, 1.0 mmol g^{-1}).

NMR Experiments

^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{51}V and 2D NMR spectroscopy were performed using a Bruker AVANCE 300 MHz or 500 MHz instrument with chemical shift (δ) referenced to the residual solvent peak or externally to 85% H_3PO_4 (0 ppm) or $V(O)Cl_3$ (0 ppm). For quantitative ^{1}H-^{13}C HSQC experiments (q-HSQC), the spectra were acquired at room temperature with the Bruker AVANCE 500 MHz spectrometer equipped with Broadband Inverse Probe (BBI) with z-gradient. 100 mg of organosolv lignin was dissolved in 1 mL of DMSO-d_6 in order to obtain

quantitative data. For q-HSQC, the pulse program was obtained from the reported method.[6] The spectral width was set to 12 - 0 ppm and 170 - 0 ppm for ^{1}H and ^{13}C dimensions, respectively. For quantitative data, the recycle delay was set to 5 s. The number of collected points was 2048 for ^{1}H dimension. The number of scans were 88 with 256 increments for a total time of approximately 33 hours. The squared sine, QSINE, function with a sine bell shift of 2 was applied in both dimensions. Quantitative ^{31}P NMR spectroscopy experiments were carried out following the reported procedure.[7-10] Under nitrogen atmosphere, 25 mg of organosolv lignin or the oxidized lignin residue was dissolved in 1.6:1 (v/v) of pyridine/$CDCl_3$ (500 μL) then 50 μL of TMDP was added to the solution. The reaction mixture was stirred for 10 min at room temperature and then transferred to a sealed screw-cap NMR tube. The spectrum was acquired using an inverse-gated decoupling pulse sequence, with a 90^{o} pulse angle, 25 s pulse delay and 256 scans. Chromium(III) tris(acetylacetonate) and cyclohexanol were used as relaxation reagent and internal standard, respectively. The spectrum was calibrated using the internal standard chemical shift at 145.2 ppm. All spectra were processed using TopSpin 3.0.

Procedure for the Catalytic Oxidation of Organosolv Lignin

For oxovanadium catalysts **1** and **2**, 50 mg of organosolv lignin was dissolved in EtOAc, *n*-butyl acetate or THF and then transferred to a 24-well plate vial containing 10 wt. % of catalyst and 10 wt. % of base heated to 100 ^{o}C. For the CuX/TEMPO **4** system, 50 mg of organosolv lignin, 10 wt. % CuOTf, 10 wt. % TEMPO and 100 wt. % 2,6-lutidine were dissolved in DMF and then transferred to a 24-well plate heated to 100 ^{o}C. For the cobalt catalyst **6**: 50 mg of organosolv lignin, 10 wt. % **6** and 100 wt. % pyridine were dissolved in 3 mL of 1:1 (v/v) MeOH/DMSO and then transferred to a 24-well plate maintained at room temperature for 24 h. For Oxovanadium bifunctional catalyst **7**: 50 mg of organosolv lignin was dissolved in EtOAc and then transferred to a 24-well plate vial containing a 10 wt. % of a mixture of isomers **7a** and **7b** heated to 100 ^{o}C. For all of the above systems the samples were sealed in the high-pressure block and then pressurized to 827 kPa (8.2 atm) with synthetic air. The block was heated to the corresponding temperature for 18 h or 24 h and cooled down before opening. For the Chornet method: 100 mg of organosolv lignin, 135 wt. % NaOH, 5 wt. % $CuSO_4$ and 0.5 wt. % $FeCl_3$ were dissolved in THF, transferred to a 50 mL pressure reactor containing 8.2 atm of synthetic air, and subsequently heated to 160 ^{o}C for 18 h. For the tridentate Schiff base vanadium catalyst **3**: 50 mg of organosolv lignin and 10 wt. % **3** were dissolved in a solvent mixture of 8:1 (v/v)

EtOAc/THF 5 mL, then the mixture was transferred to a sealed vial under atmospheric pressure of air and heated to 80 ^{o}C for 24 h with constant stirring. For the metal-free system **5**, 100 mg of organosolv lignin, 5 wt. % 4-acetamido-TEMPO, 10 wt. % nitric acid (70%) and 10 wt. % HCl (37%) were dissolved in 10 mL of a solvent mixture of 19:1 (v/v) CH_3CN/H_2O. The mixture was transferred to a 50 mL pressure reactor containing 8.2 atm of synthetic air and then heated to 65 ^{o}C for 24 h with constant stirring. The 2D-NMR experiments were carried out by evaporating the solvent of each sample and dissolving the residue in DMSO-d_6. For GPC analysis, each sample was filtered through silica gel to eliminate traces of metal in order to protect the GPC instrument.

X-Ray Crystallography

Data collection results for compound **7** (CCDC reference number 1062663) represent the best data sets obtained in several trials for each sample. The crystals were mounted on thin glass fibers using paraffin oil. Prior to data collection crystals were cooled to 200.15 °K. Data were collected on a Bruker AXS SMART single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) APEX II CCD detector. Raw data collection and processing were performed with APEX II software package from BRUKER AXS.[11] Diffraction data for all samples were collected with a sequence of 0.3° ω scans at 0, 120, and 240° in φ. Initial unit cell parameters were determined from 60 data frames with 0.3° ω scan each collected at the different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.[12] Systematic absences in the diffraction data-set and unit-cell parameters were consistent with monoclinic **P***2$_1$/c* (№14) for compound **7**. Solutions in the centrosymmetric space groups for all compound yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2.

Asymmetric unit of structural model for compound **7** consists of one molecule of target compound located in the inversion center and one fully occupied molecule of acetonitrile crystallization solvent located in the general position of the symmetry group.

All hydrogen atoms positions were calculated based on the geometry of the related non-hydrogen atoms. All hydrogen atoms were treated as idealized contributions during the refinement. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12[13]

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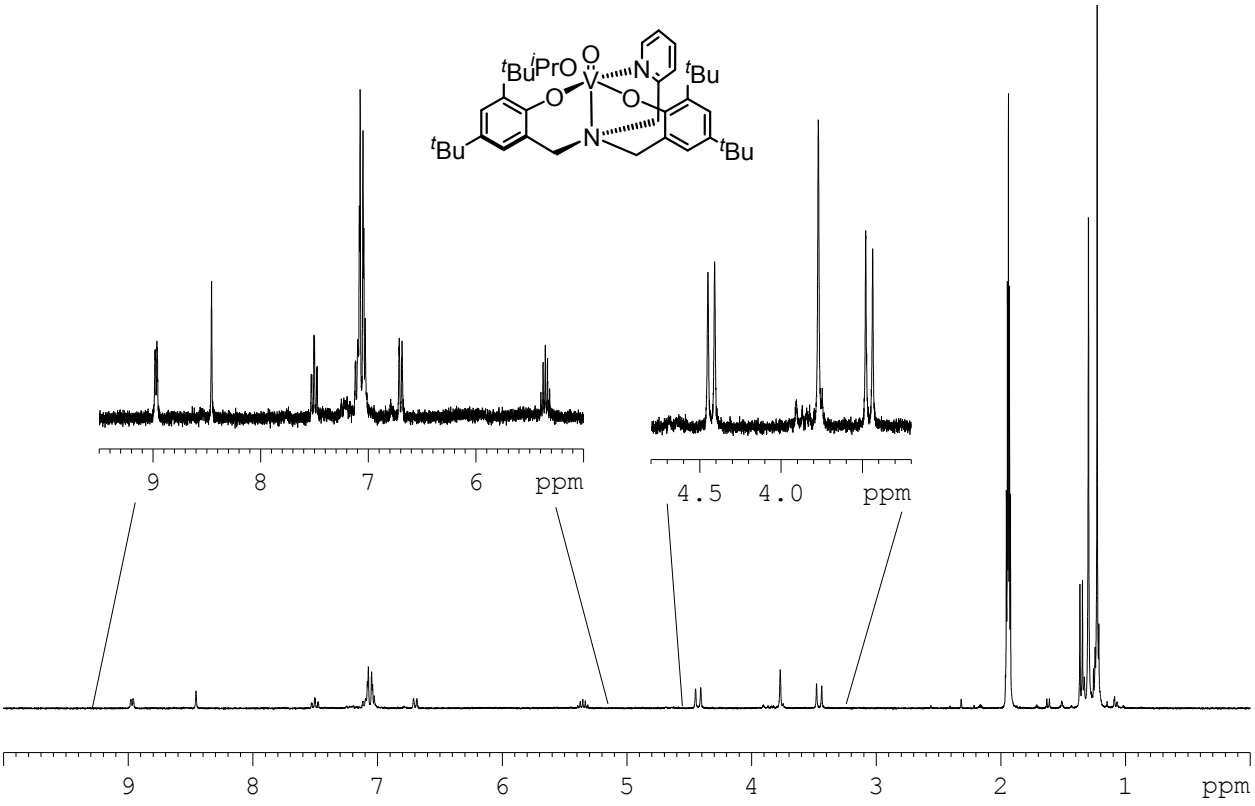

Figure S1. ^{1}H NMR (300 MHz, CD_3CN) of **7a**.

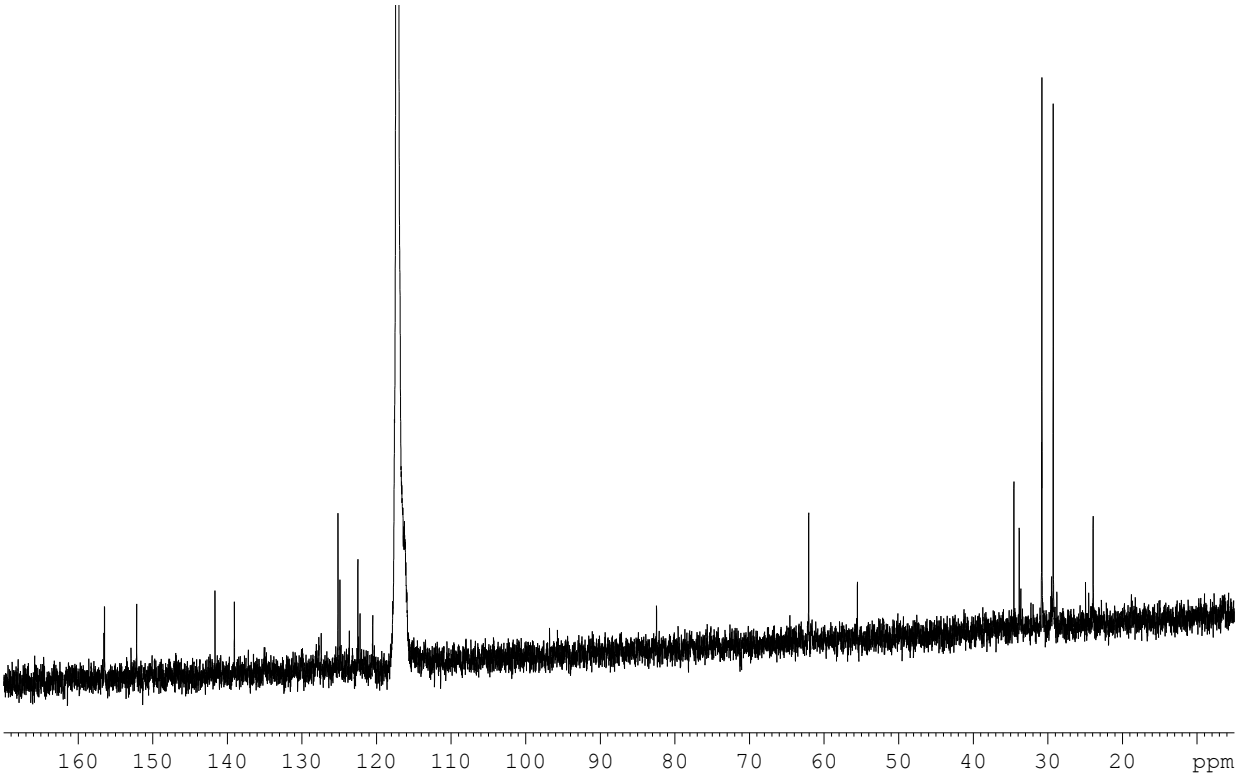

Figure S2. $^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_3CN) of **7a**.

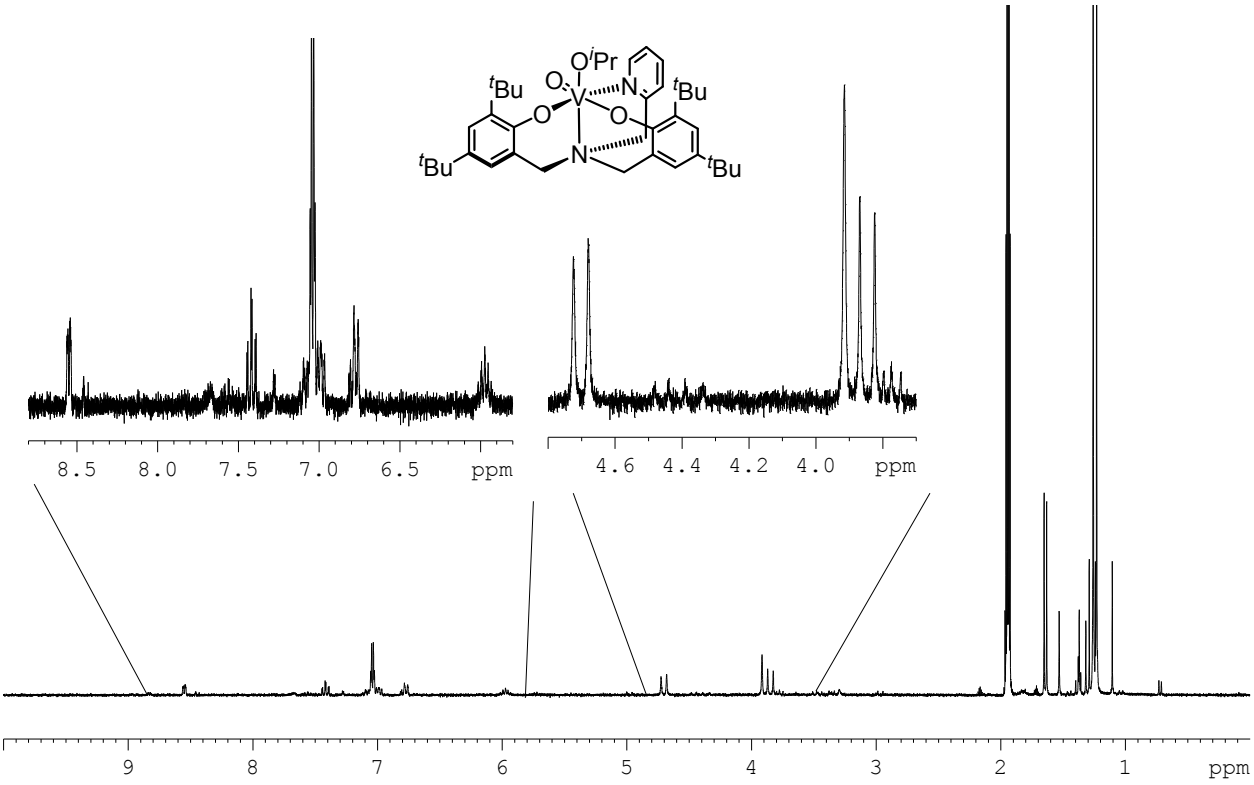

Figure S3. ^{1}H NMR (300 MHz, CD_3CN) of **7b**.

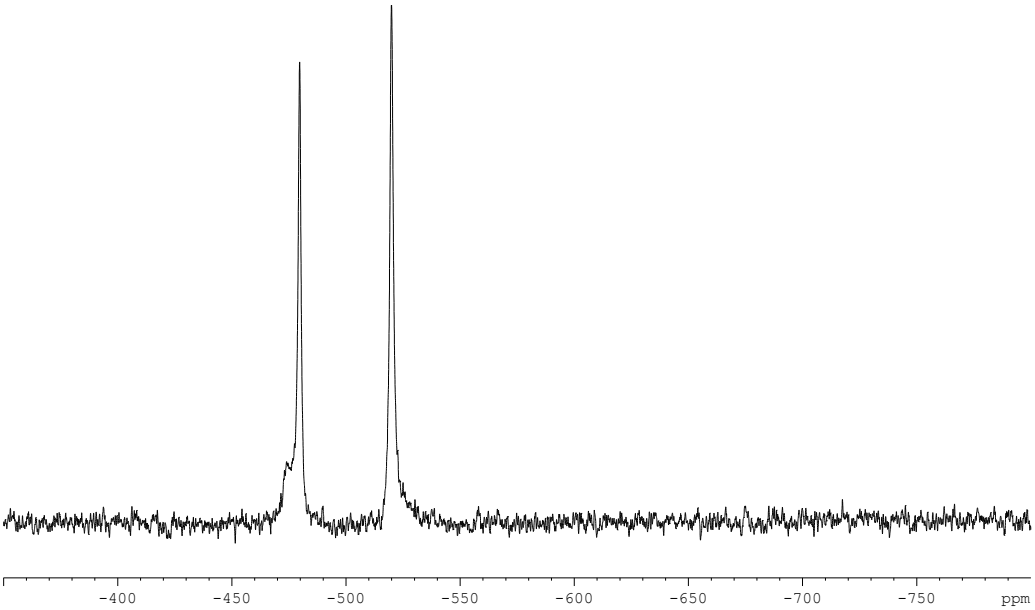

Figure S4. ^{51}V NMR (78.9 MHz, CD_3CN) of the mixture of **7a** and **7b**.

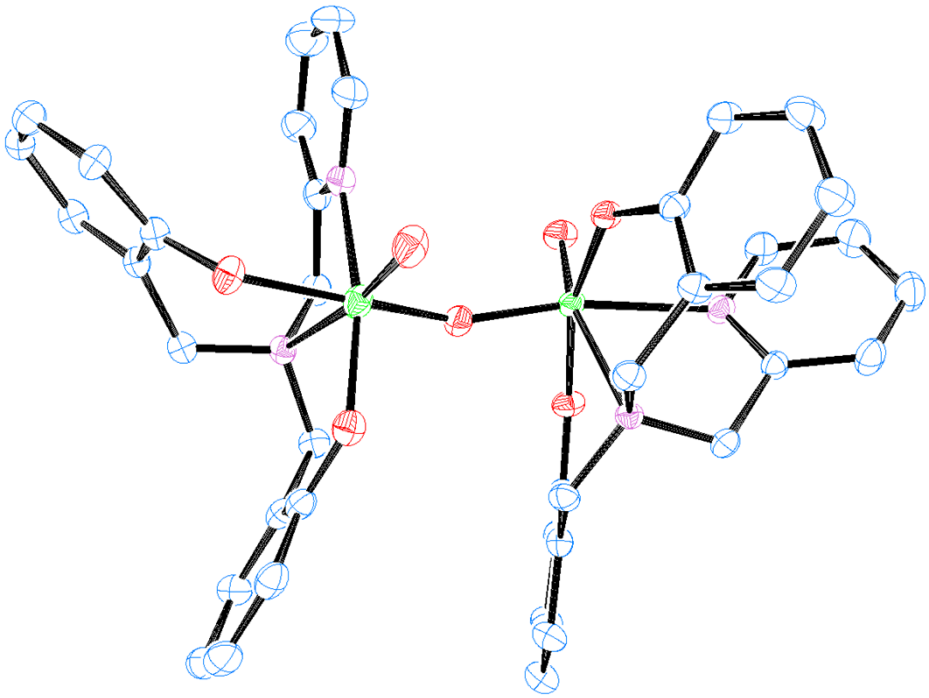

Figure S5. ORTEP representation of **7** with ellipsoids at 35% probability, hydrogen atoms, *tert*-butyl and second assymetric structure are omitted for clarity.

Table S1. Crystallographic data for **7**.

	7
formula	$C_{76}H_{106}N_6O_7V7$
fw	1371.54
a (Å)	14.6421(4)
b (Å)	17.5486(4)
c (Å)	15.7326(4)
α (deg)	90
β (deg)	113.6928(11)
γ (deg)	90
crystal system	monoclinic
Space group	P 21/n
V (Å^3)	3701.74(16)
D_c (g cm^{-1})	1.182
μ (mm^{-1})	0.307
Z	2
F(000)	1412.0
T/K	200.0
R_1 [I>2σ(I)]	0.0369(8127)
wR_1 [I>2σ(I)]	0.1030(9146)

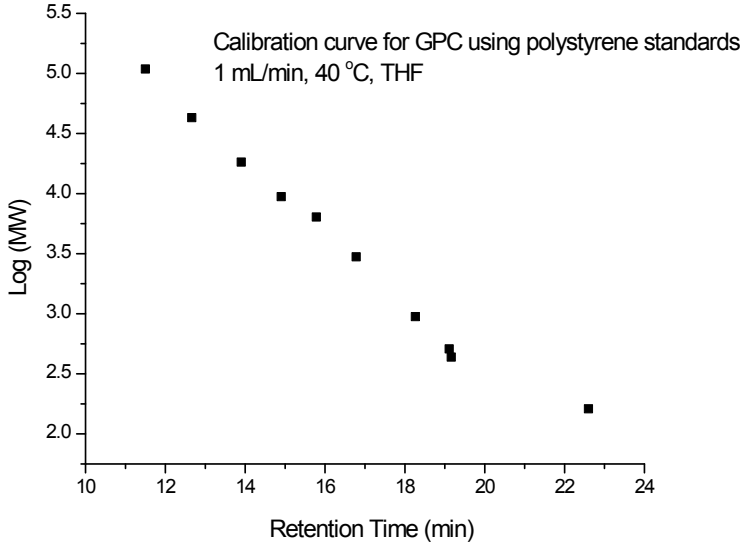

Figure S6. GPC calibration curve using polystyrene standards (Mw = 109,000-162 Da).

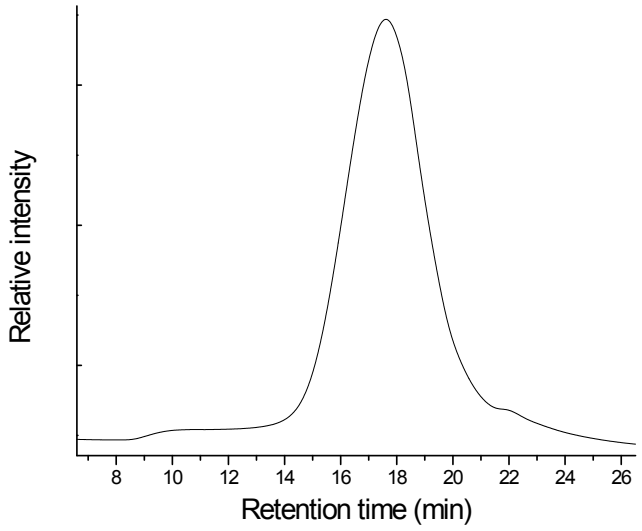

Figure S7. GPC chromatogram (THF solvent, elution rate: 1 mL/min, 254.4 nm detection) for organosolv lignin.

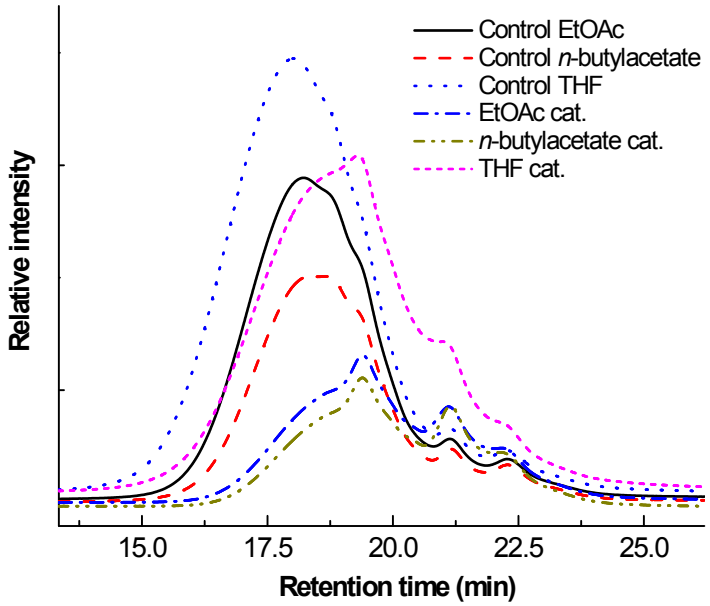

Figure S8. GPC chromatograms (THF solvent, elution rate: 1 mL/min, 254.4 nm detection) for the catalytic oxidation of organosolv lignin; solvent screening using 10 wt. % catalyst **2** and 10 wt. % Et_3N compared with the control experiment (no catalyst). For all runs: temperature = 100 ^oC; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

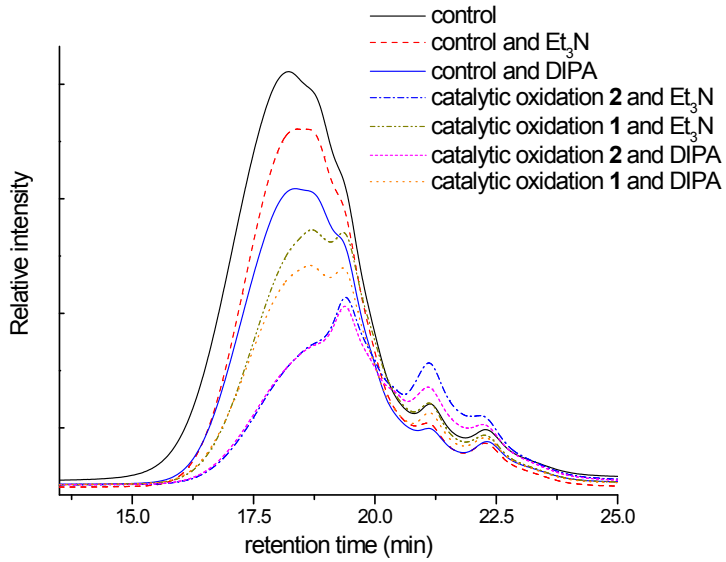

Figure S9. GPC chromatograms (THF solvent, elution rate: 1 mL/min, 254.4 nm detection) for the catalytic oxidation of organosolv lignin using different bases; 10 wt. % catalyst **1** or **2** and 10 wt. % base compared with the control experiment (no catalyst). For all runs: solvent = EtOAc; temperature = 100 ^oC; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

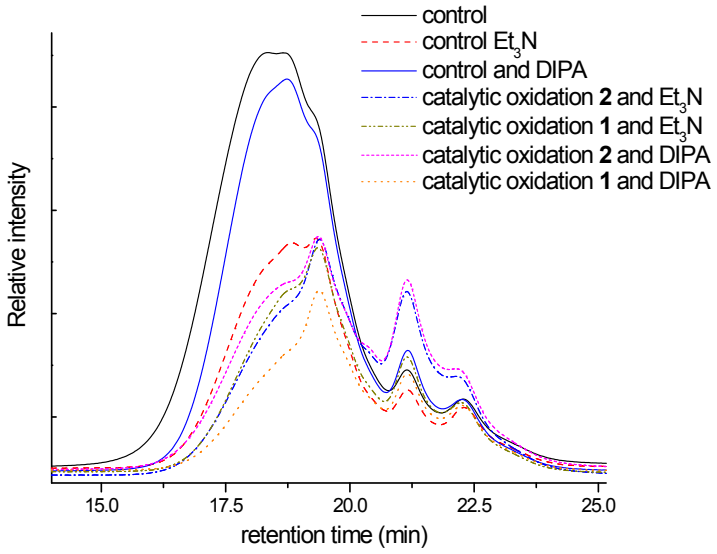

Figure S10. GPC chromatograms (THF solvent, elution rate: 1 mL/min, 254.4 nm) for the catalytic oxidation of organosolv lignin using different bases; 10 wt. % catalyst **1** or **2** and 10 wt. % base compared with the control experiment (no catalyst). For all runs: solvent = *n*-butyl acetate; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

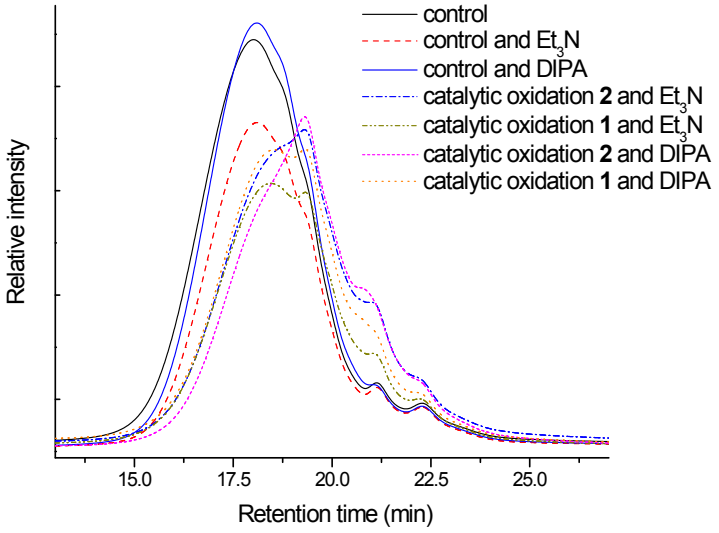

Figure S11. GPC chromatograms (THF solvent, elution rate: 1 mL/min, 254.4 nm detection) for the catalytic oxidation of organosolv lignin using different bases; 10 wt. % catalyst **1** or **2** and 10 wt. % base compared with the control experiment (no catalyst). For all runs: solvent = THF; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

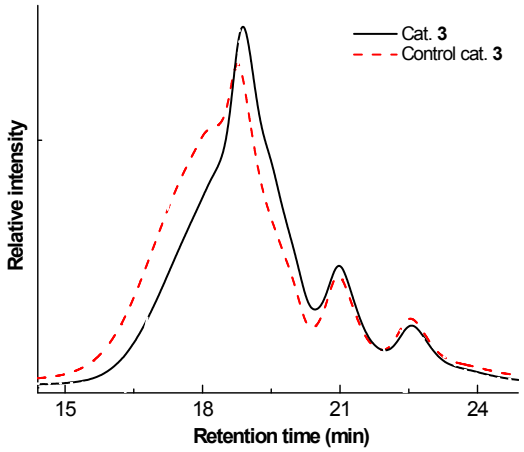

Figure S12. GPC chromatograms (THF solvent, elution rate: 1 mL/min, 254.4 nm detection) for the reaction of organosolv lignin using catalyst **3**; 10 wt. % **3**. For all runs: solvent = 8:1 (v/v) EtOAc/THF; temperature = 80 °C; sealed vial under atmospheric pressure of air; reaction time = 24 h.

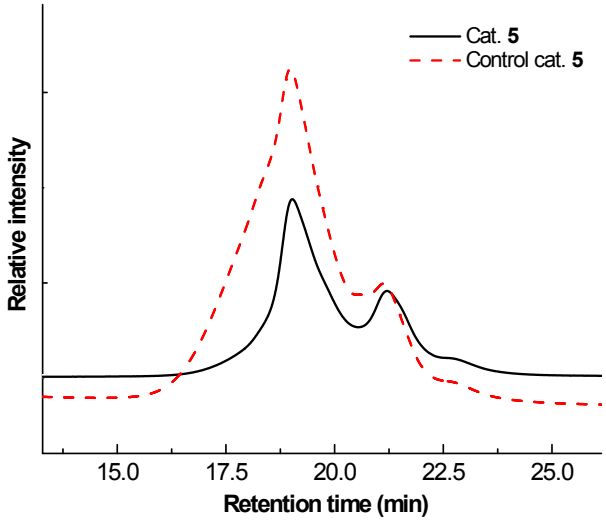

Figure S13. GPC chromatograms (THF solvent, elution rate: 1 mL/min, 254.4 nm detection) for the reaction of organosolv lignin using the metal-free system **5**, 5 wt. % 4-acetamido-TEMPO, 10 wt. % nitric acid (70%), 10 wt. % HCl (37%). For all runs: solvent = 19:1 (v/v) CH_3CN/H_2O; temperature = 65 °C; pressure of synthetic air = 8.2 atm; reaction time = 24 h.

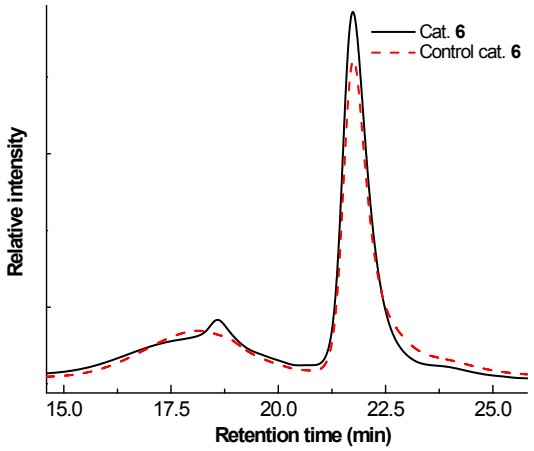

Figure S14. GPC chromatograms (THF solvent, elution rate: 1 mL/min, 254.4 nm detection) for reaction of organosolv lignin using catalyst **6**; 10 wt % **6** and 100 wt. % pyridine. For all runs: solvent = 1:1 (v/v) MeOH/DMSO; temperature = 100 ^{o}C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

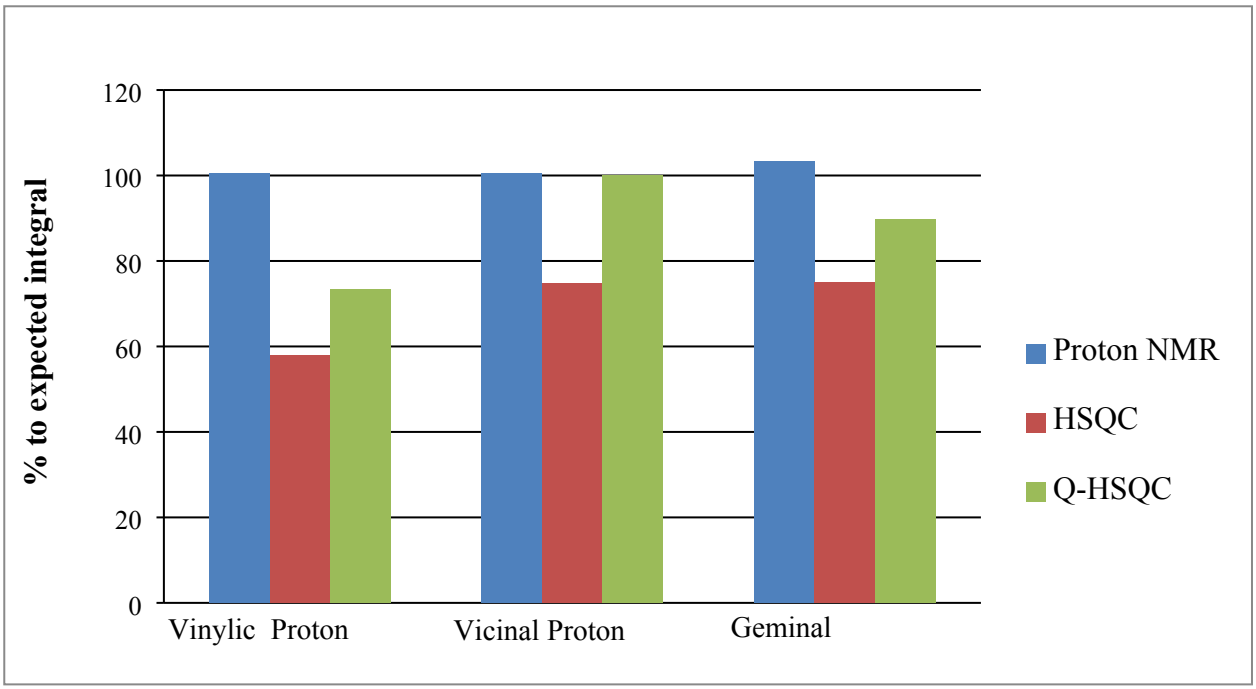

Figure S15. Comparison of relative integrals of ^{1}H, HSQC, and q-HSQC NMR spectra of cyclohexene in $CDCl_3$. Precision of the q-HSQC method was determined by measuring the integrals of cross-peaks of cyclohexene four times with the relative standard error being less than 1.4%. The accuracy of q-HSQC was evaluated by comparing the percentage of protons integrated for cyclohexene to ^{1}H-NMR.

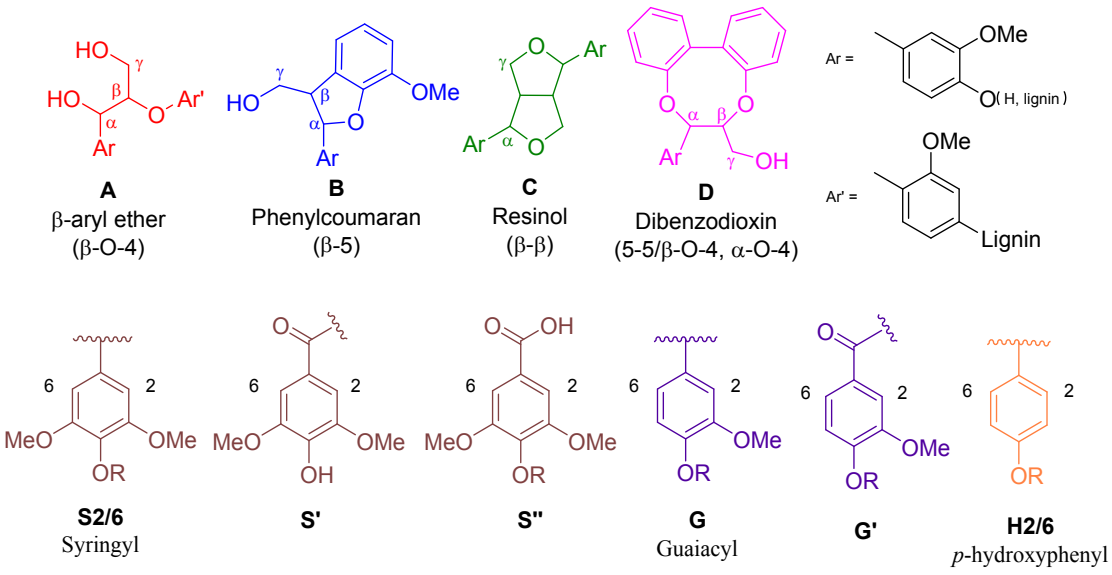

Figure S16. Lignin linkages observed by q-HSQC NMR experiments.

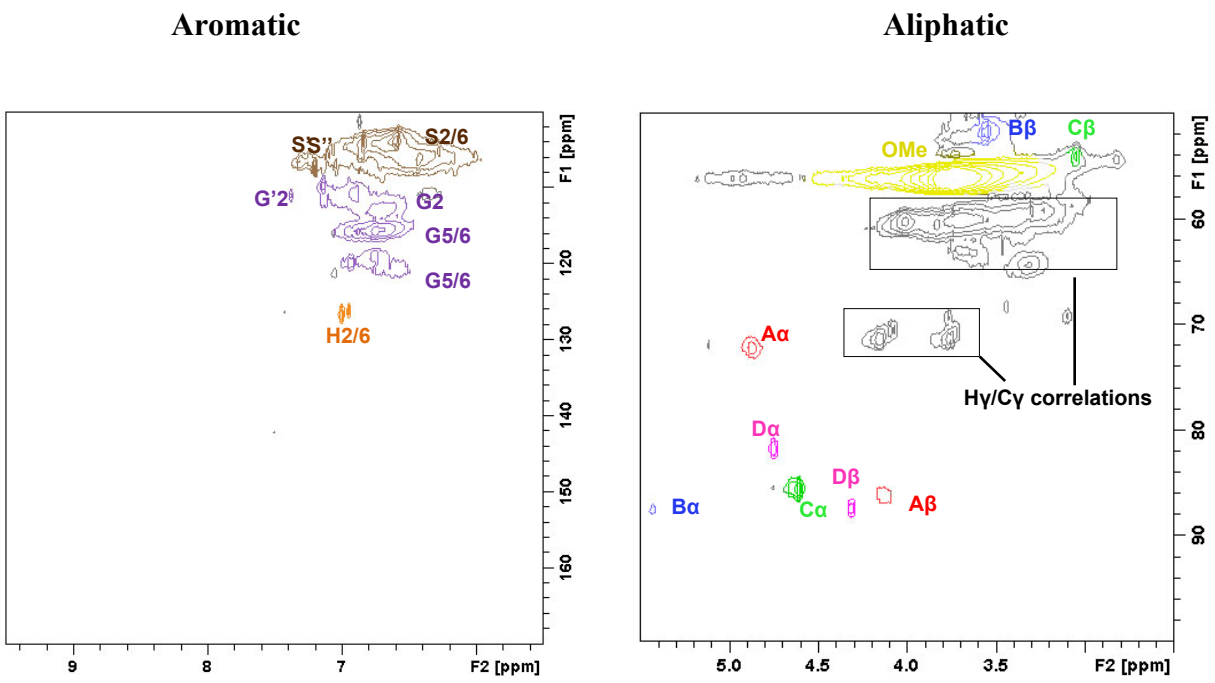

Figure S17. q-HSQC NMR spectrum (500 MHz; DMSO-d_6) of pure organosolv lignin.

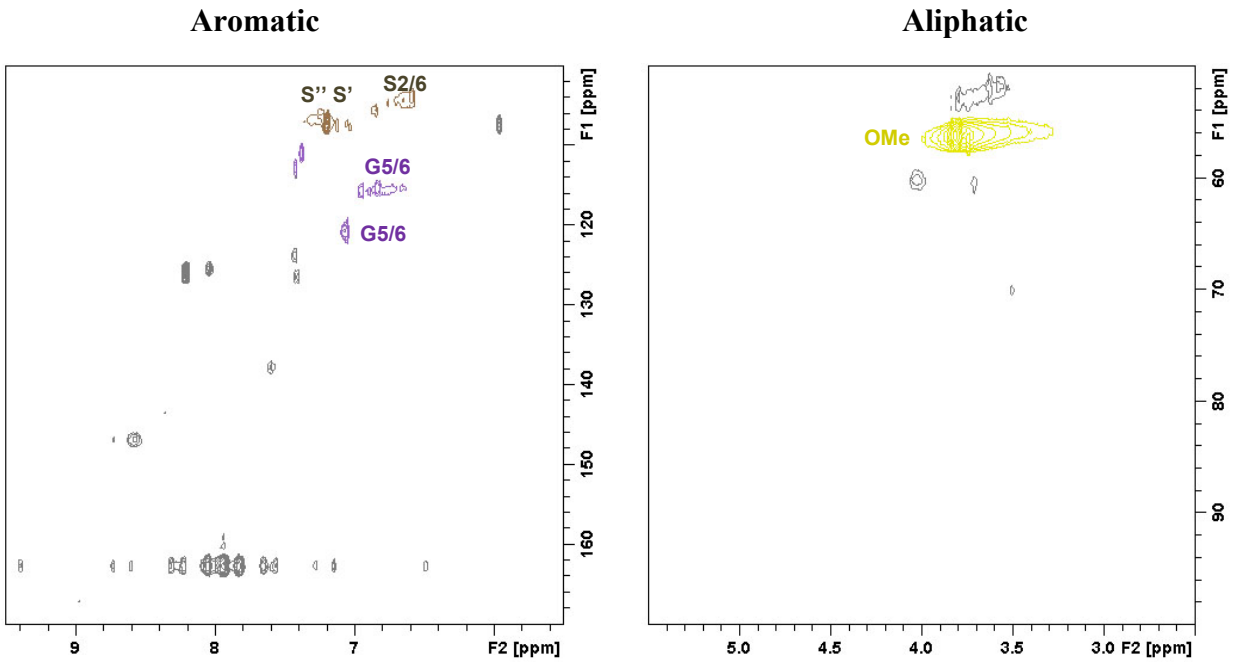

Figure S18. q-HSQC NMR spectrum (500 MHz; DMSO-d_6) for the catalytic oxidation of organosolv lignin using 10 wt. % **1** and 10 wt. % Et_3N. For all runs: solvent = EtOAc; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

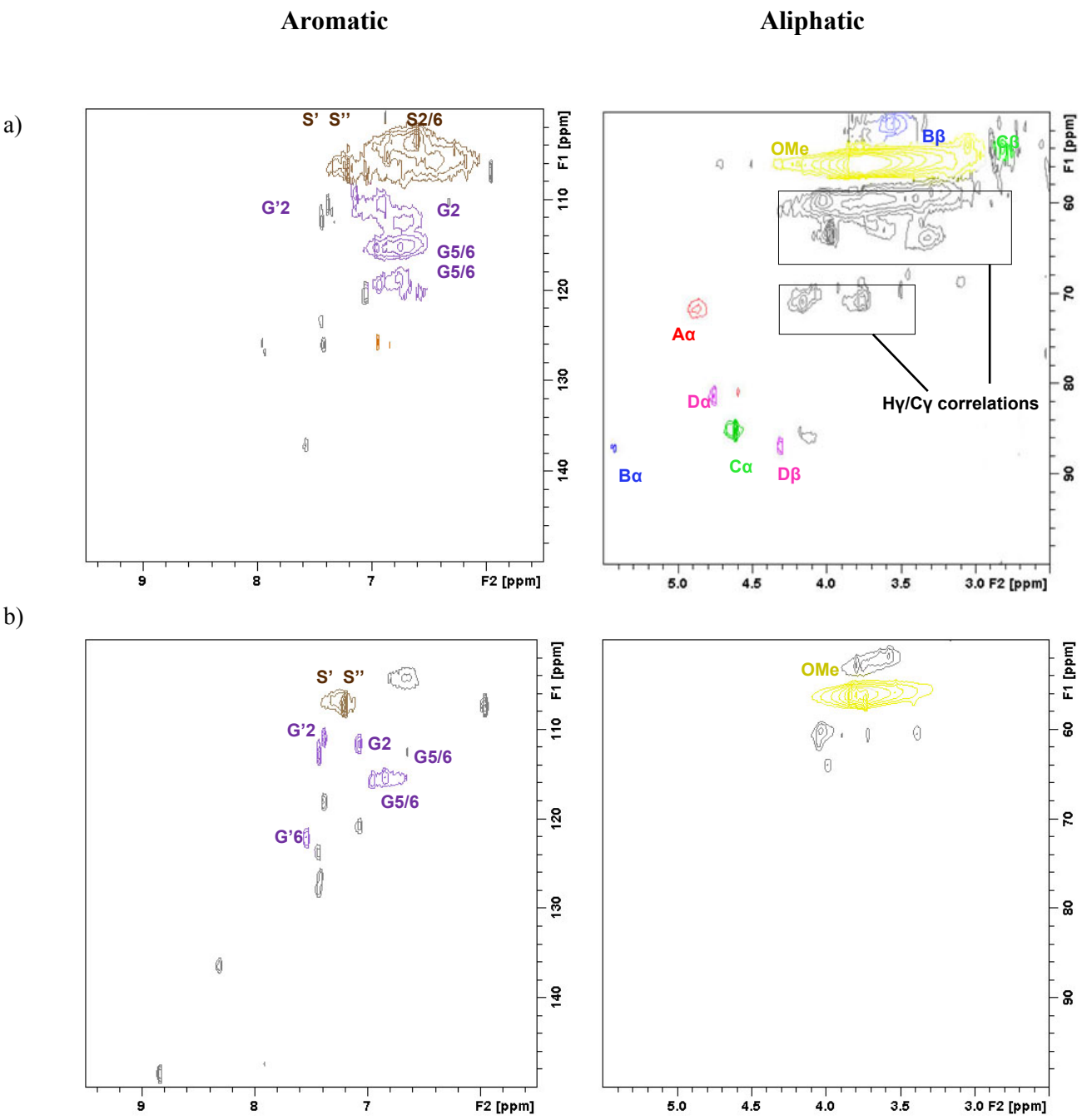

Figure S19. q-HSQC NMR spectra (500 MHz; DMSO-d_6) of organosolv lignin for a) control experiment (no catalyst **2**) and b) catalytic oxidation using 10 wt. % **2** and 10 wt. % Et_3N. For all runs: solvent: *n*-butyl acetate; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

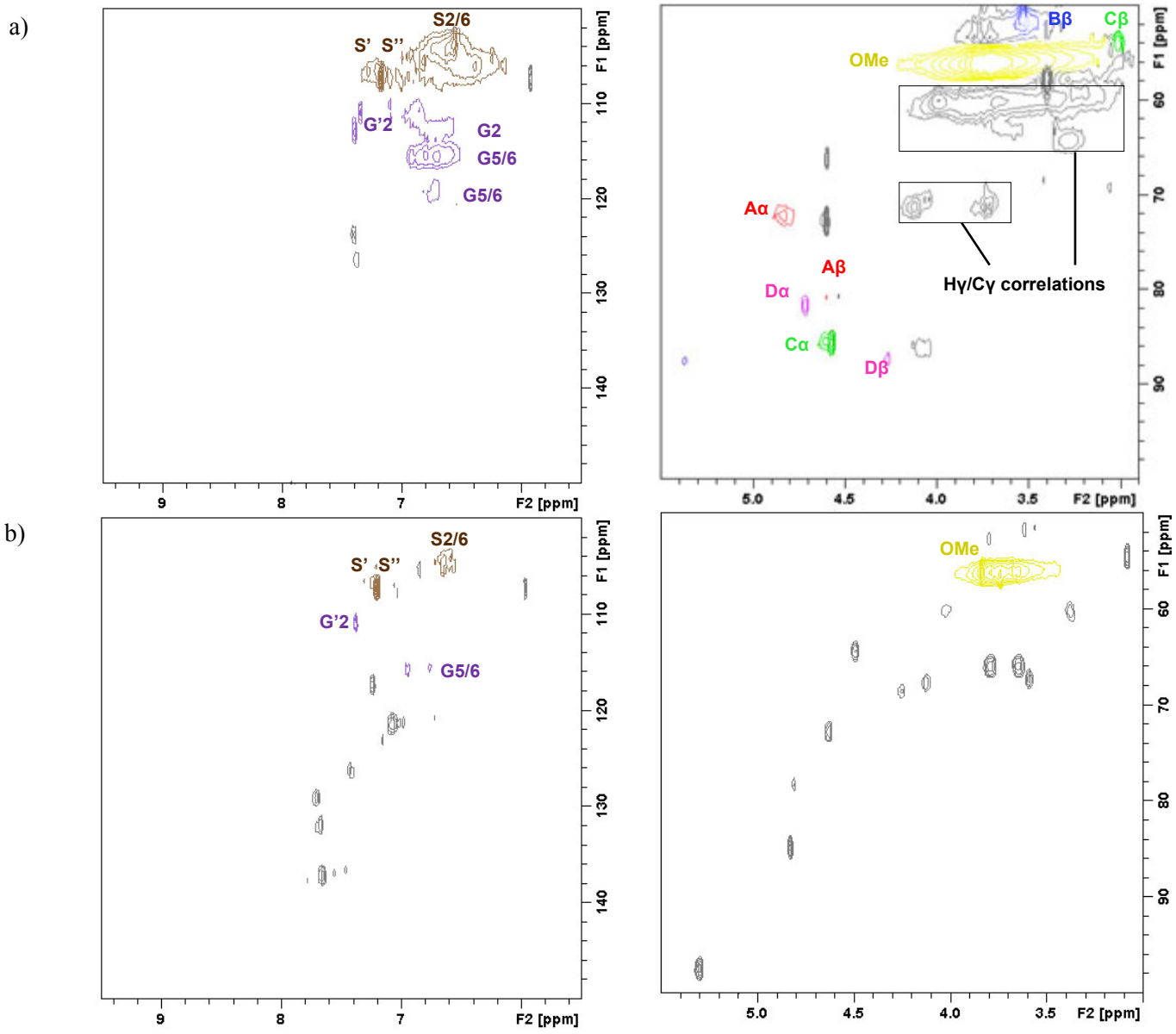

Figure S20. q-HSQC NMR spectra (500 MHz; DMSO-d_6) of organosolv lignin for a) control experiment (no catalyst, TEMPO or base) and b) catalytic oxidation with 10 wt. % CuOTf, 10 wt. % TEMPO and 100 wt. % 2,6-lutidine. For all runs: solvent = DMF; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h. Some of the correlations may be affected by paramagnetism of copper(II) traces.

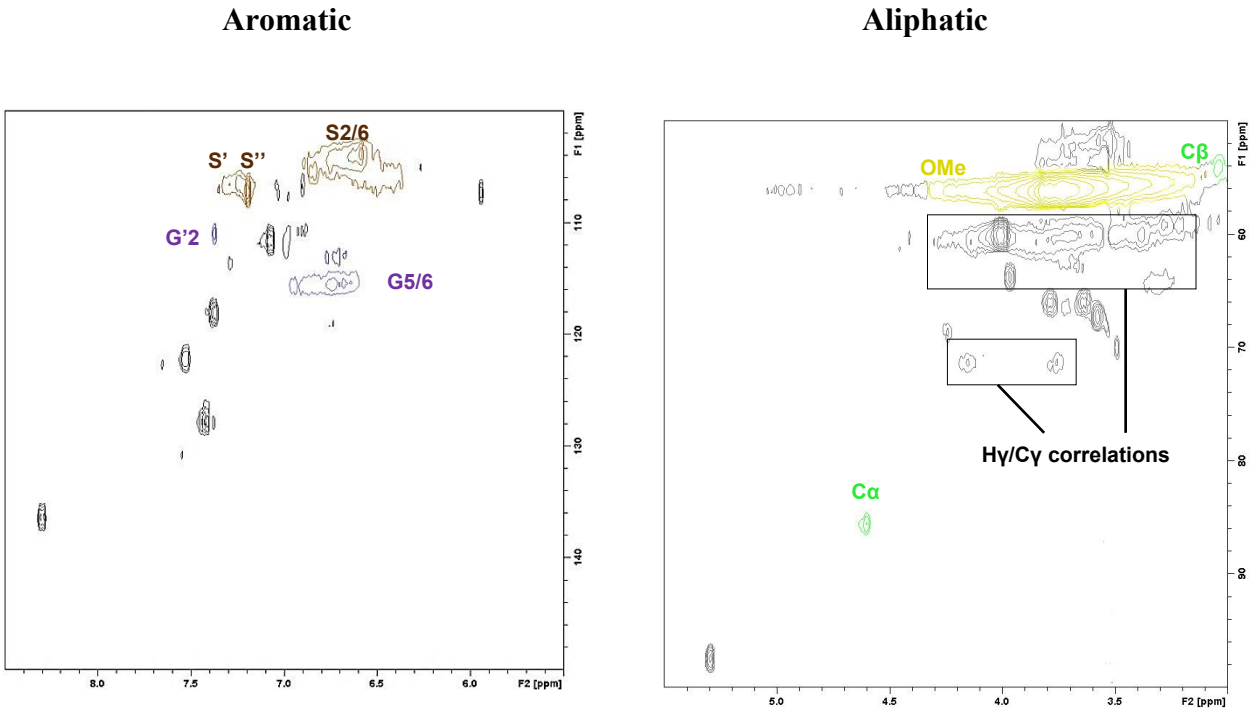

Figure S21. q-HSQC NMR spectrum (500 MHz; DMSO-d_6) for the reaction of organosolv lignin using 10 wt. % **2** in the absence of base. For all runs: solvent = 8:1 (v/v) EtOAc/THF; temperature = 80 °C; atmospheric pressure of air; reaction time = 24 h.

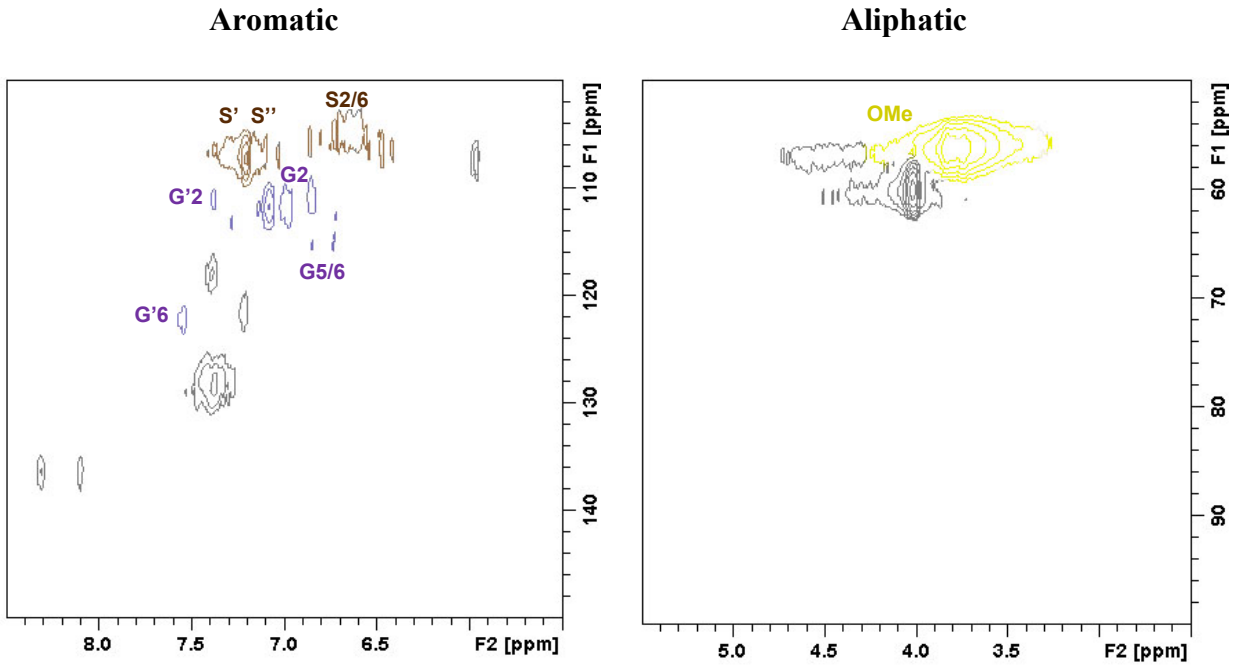

Figure S22. q-HSQC NMR spectrum (500 MHz; DMSO-d_6) for the catalytic oxidation of organosolv lignin using 10 wt. % **2**, 10 wt. % Et_3N. For all runs: solvent = EtOAc; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 4 h.

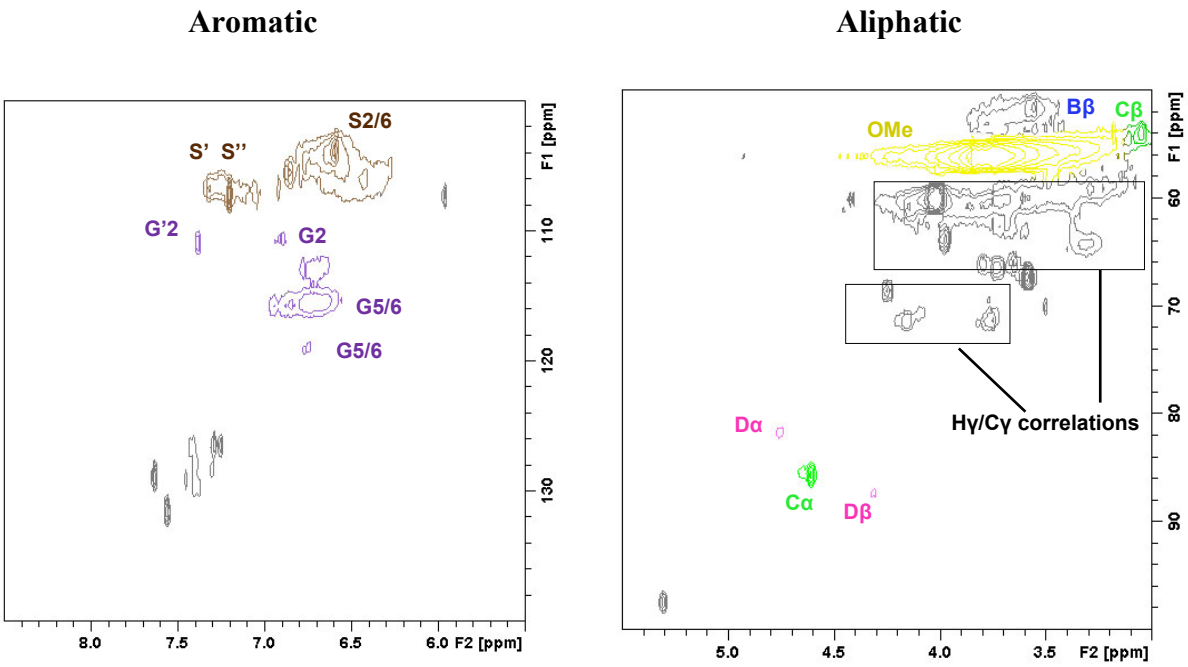

Figure S23. q-HSQC NMR spectrum (500 MHz; DMSO-d_6) of the reaction of organosolv lignin using catalyst **3**; 10 wt. % **3**. For all runs: solvent = 8:1 (v/v) EtOAc/THF; temperature = 80 ^{o}C; sealed vial under atmospheric pressure of air; reaction time = 24 h.

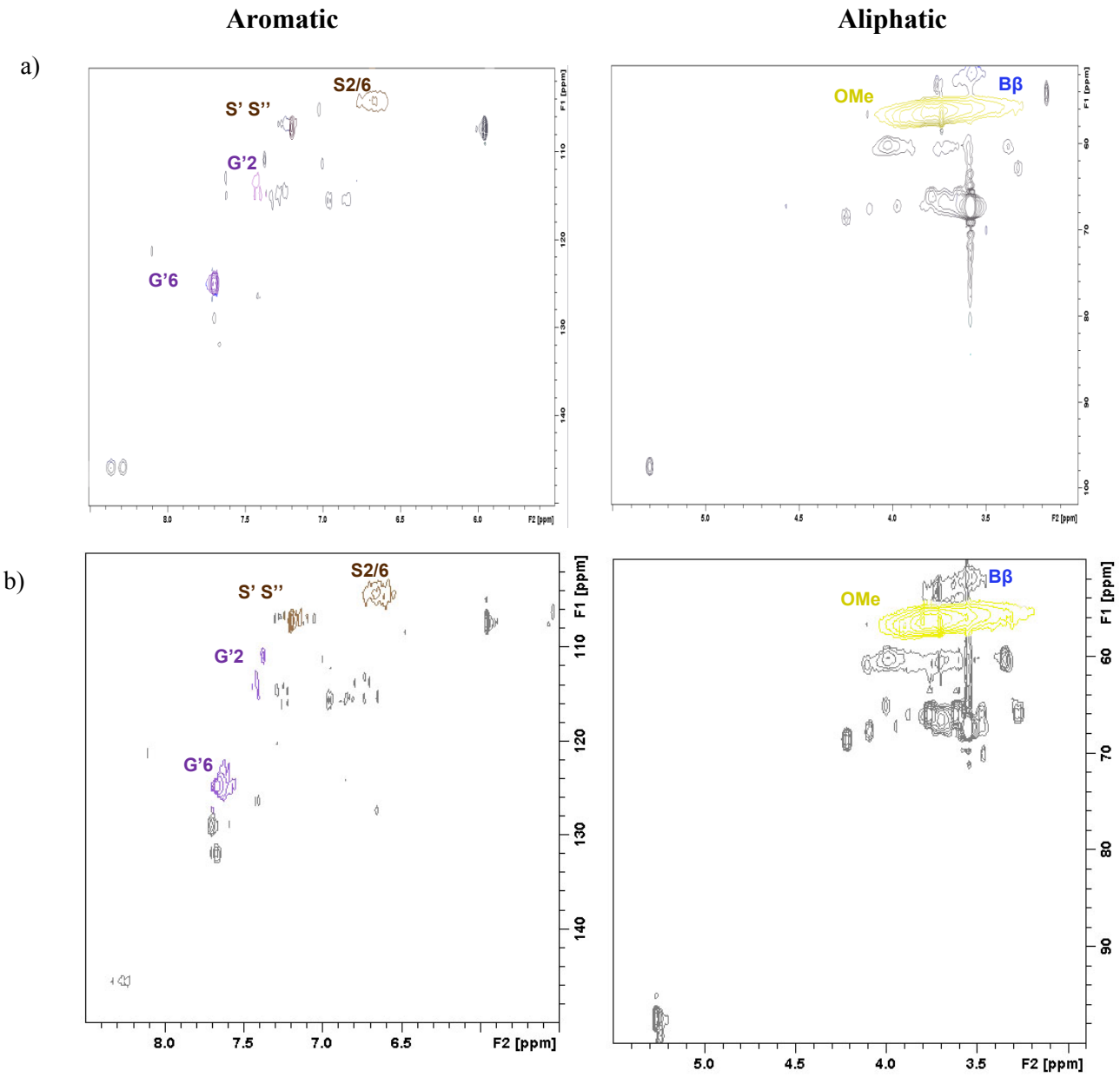

Figure S24. q-HSQC NMR spectrum (500 MHz; DMSO-d_6) of the reaction of organosolv lignin for a) control experiment (no 4-acetamido-TEMPO) and b) 5 wt. % 4-acetamido-TEMPO, 10 wt. % HNO_3 (70%), 10 wt. % HCl (37%). For all runs: solvent = 19:1 (v/v) CH_3CN/H_2O; temperature = 65 °C; pressure of synthetic air = 8.2 atm; reaction time = 24 h.

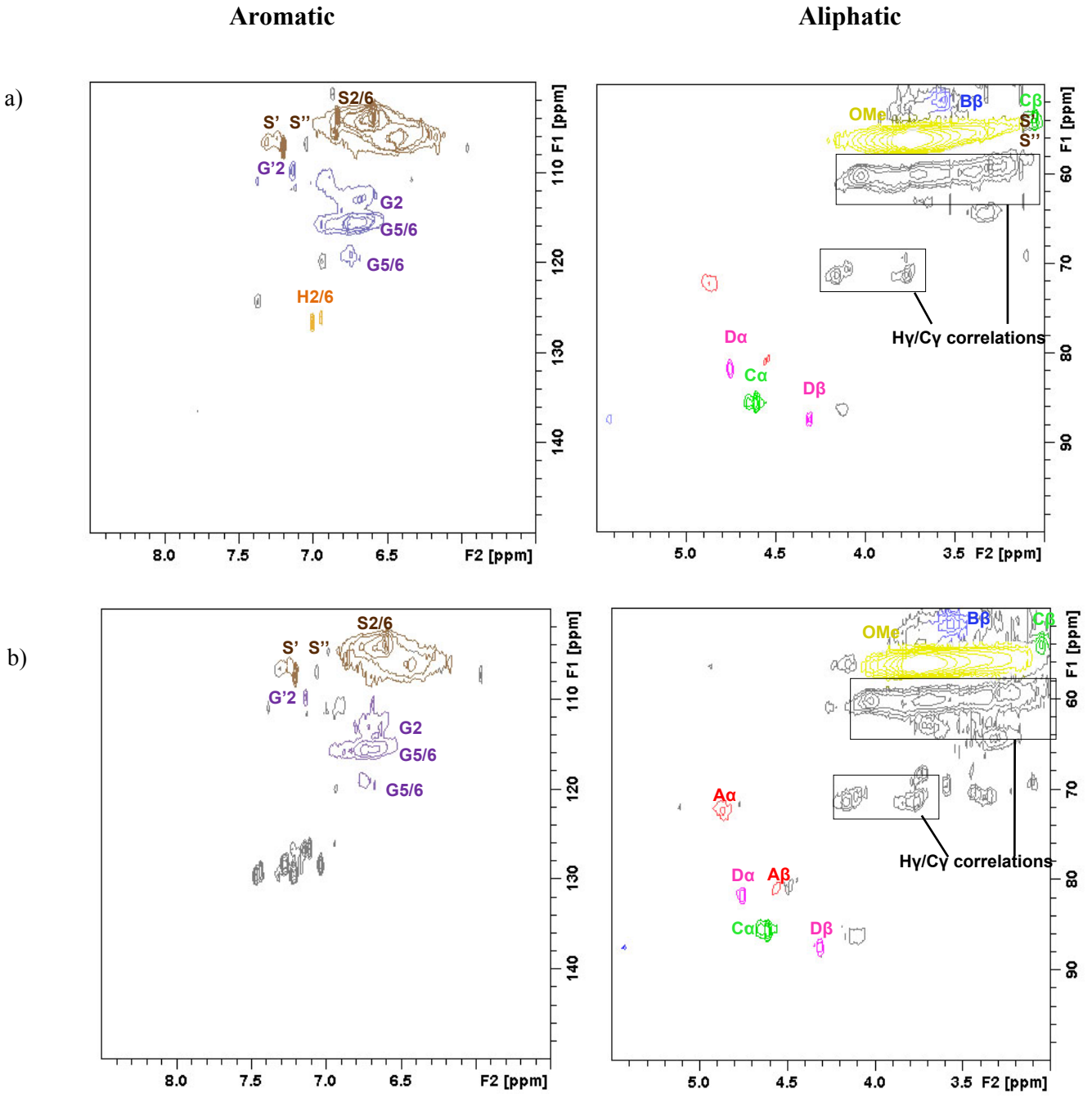

Figure S25. q-HSQC NMR spectrum (500 MHz; DMSO-d_6) of the reaction of organosolv lignin for a) control experiment (no catalyst **6**) and b) using 10 wt. % **6** and 100 wt. % pyridine. For all runs: solvent = 1:1 (v/v) MeOH/DMSO; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

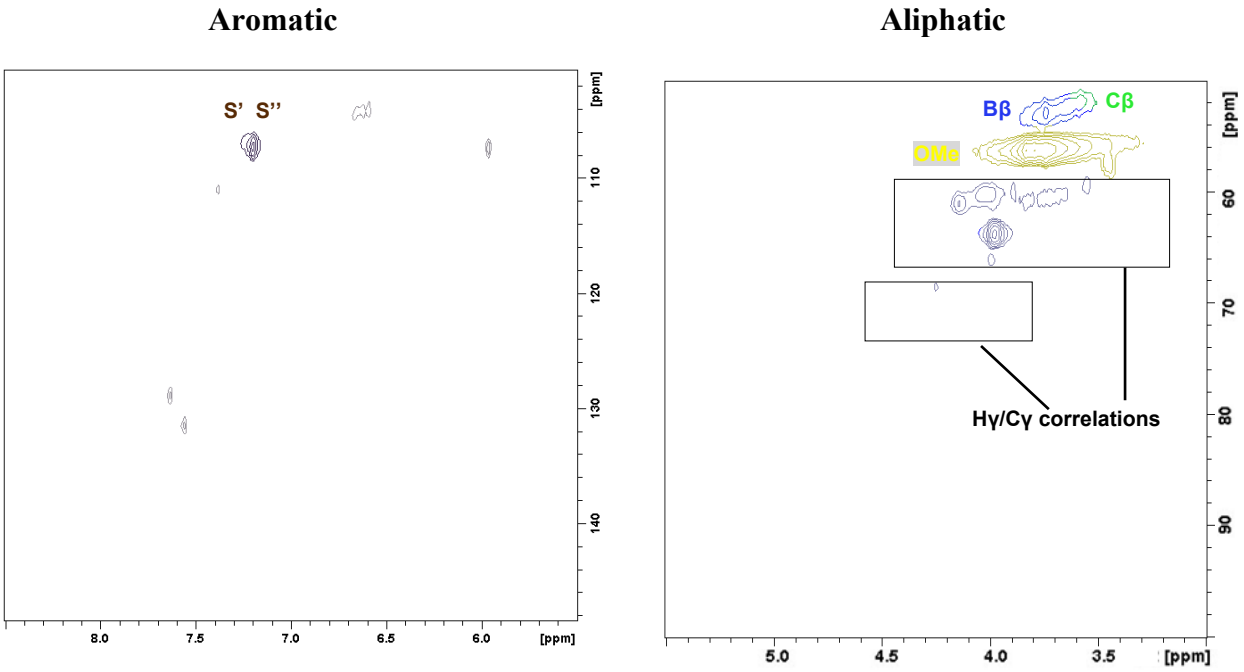

Figure S26. q-HSQC NMR spectrum (500 MHz; DMSO-d_6) of the reaction of organosolv lignin for 10 wt. % **7**. For all runs: solvent = EtOAc; temperature = 100 ^{o}C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

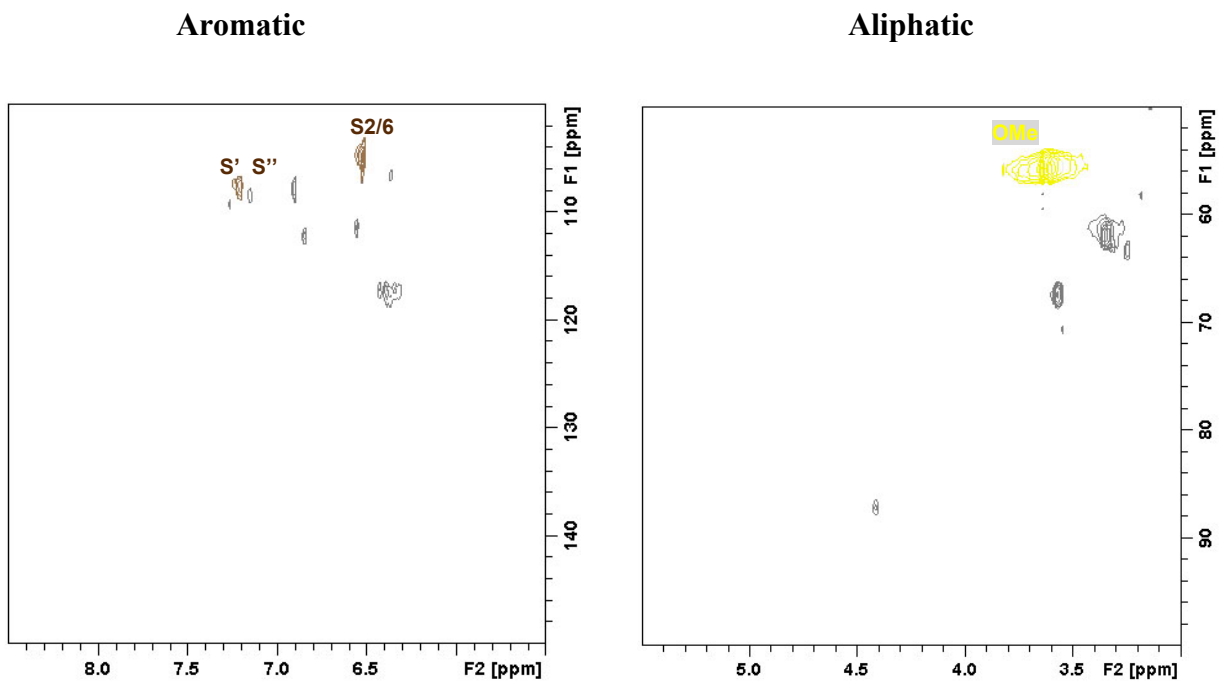

Figure S27. q-HSQC NMR spectrum (500 MHz; DMSO-d_6) of the reaction of organosolv lignin using the Chornet method (135 wt. % NaOH, 5 wt. % $CuSO_4$ and 0.5 wt. % $FeCl_3$). For all runs: solvent = THF; temperature = 100 ^oC; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

Aromatic **Aliphatic**

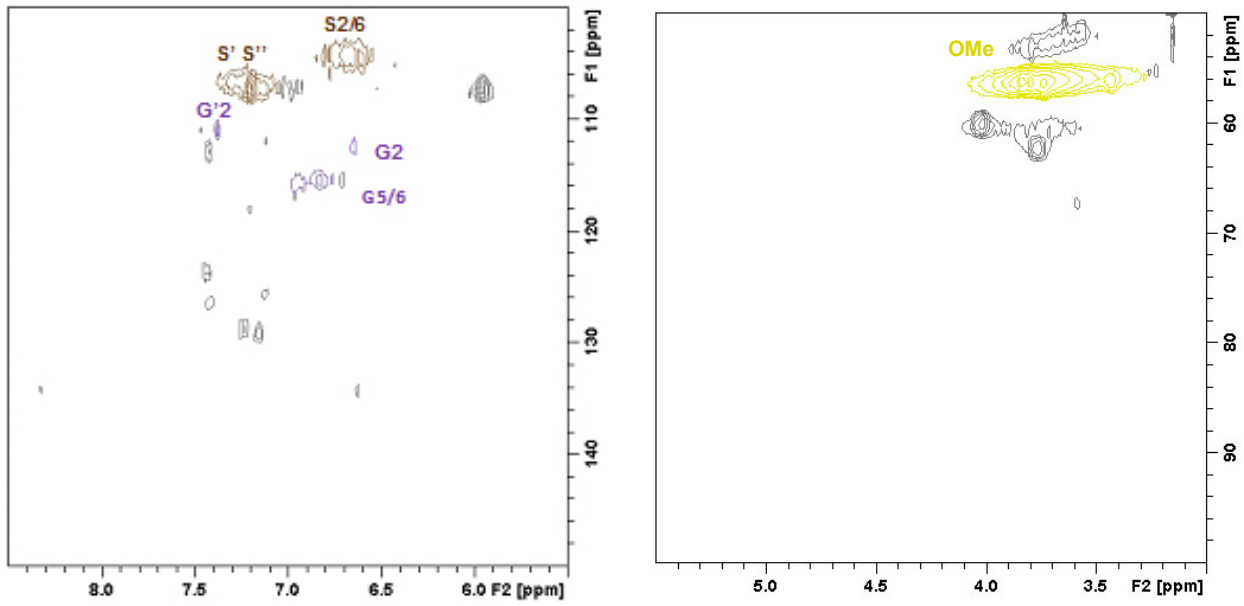

Figure S28. q-HSQC NMR spectrum (500 MHz; DMSO-d_6) of the catalytic oxidation of organosolv lignin using 10 wt. % **2**, 10 wt. % Et_3N. For all runs: solvent = DMSO; temperature = 100 ^oC; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

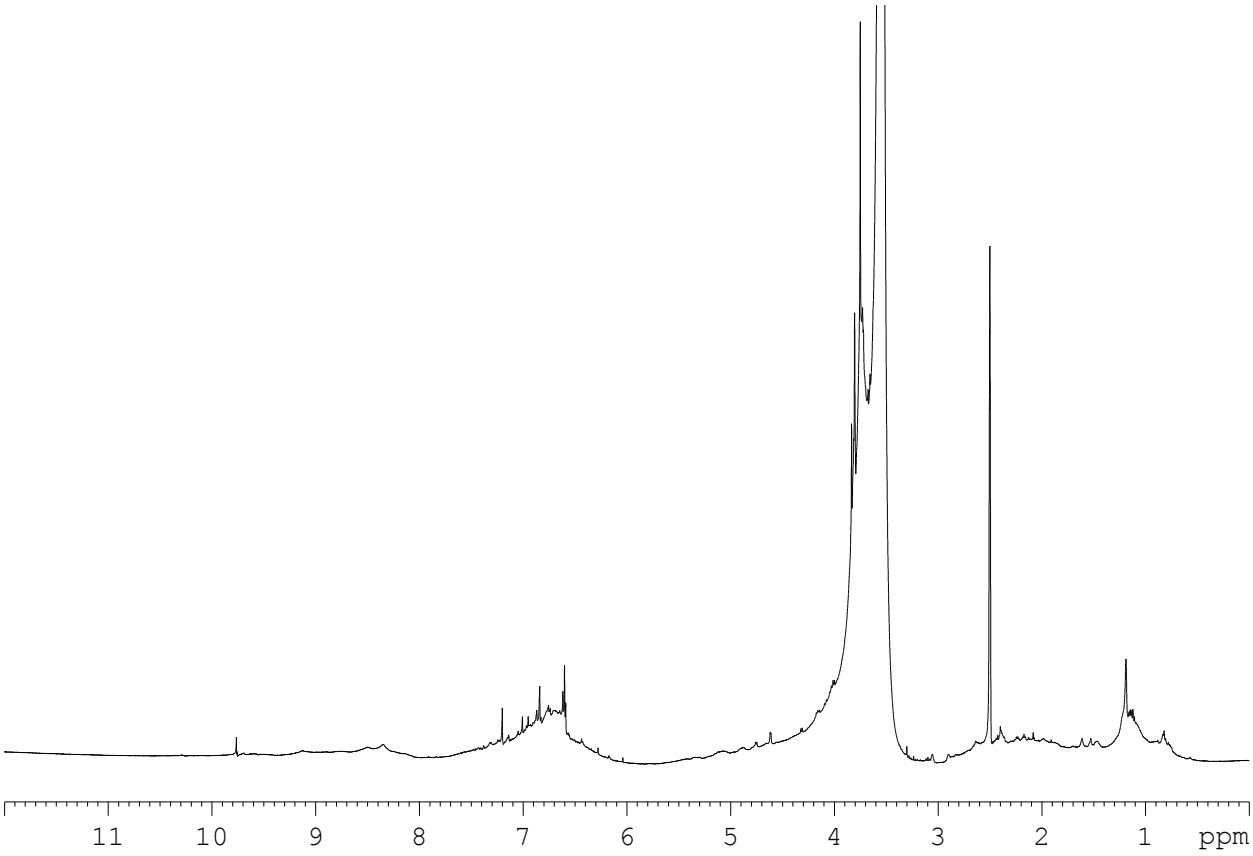

Figure S29. ^{1}H NMR spectrum (500 MHz; DMSO-d_6) of organosolv lignin

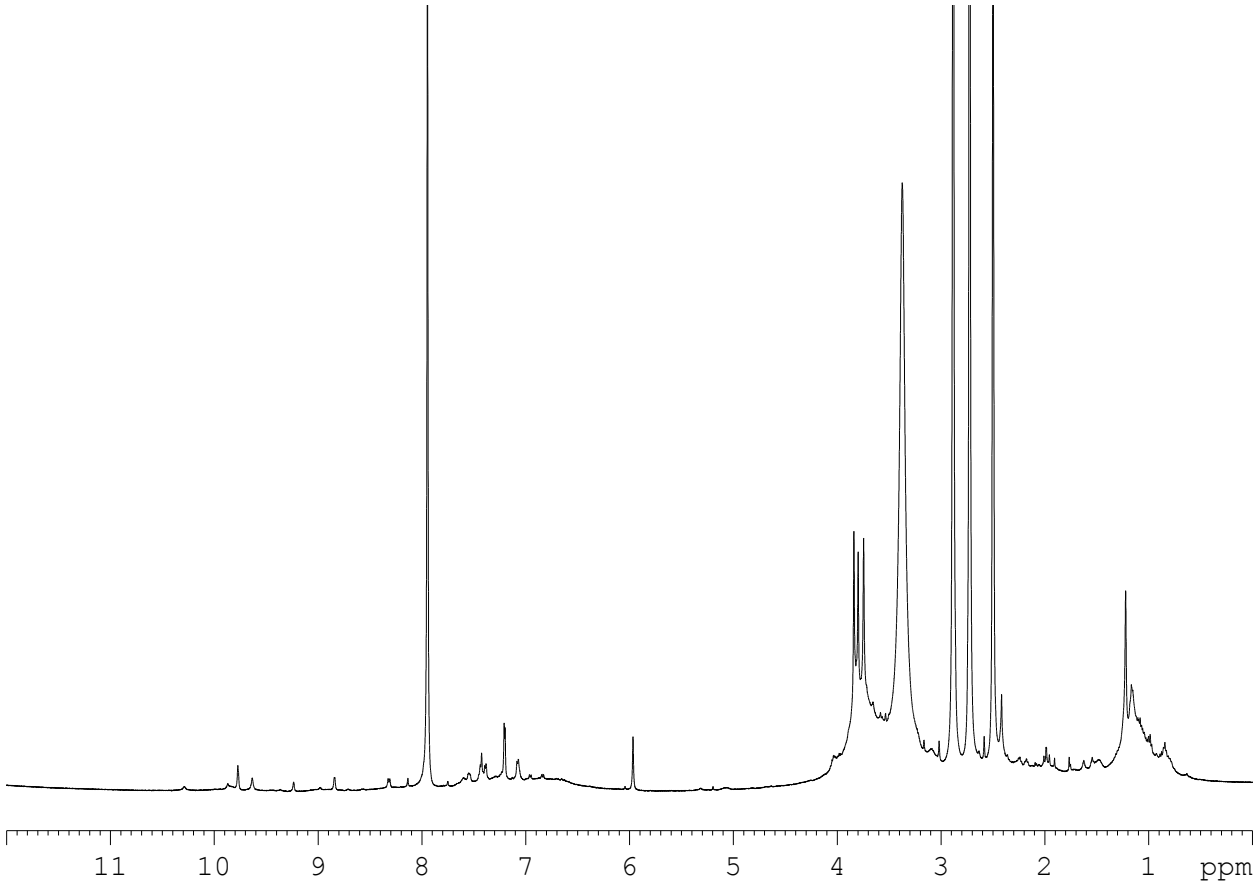

Figure S30. ^{1}H NMR spectrum (500 MHz; DMSO-d_6) of the catalytic oxidation of organosolv lignin using 10 wt. % **2** and 10 wt. % Et_3N. For all runs: solvent = EtOAc; temperature = 100 ^{o}C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

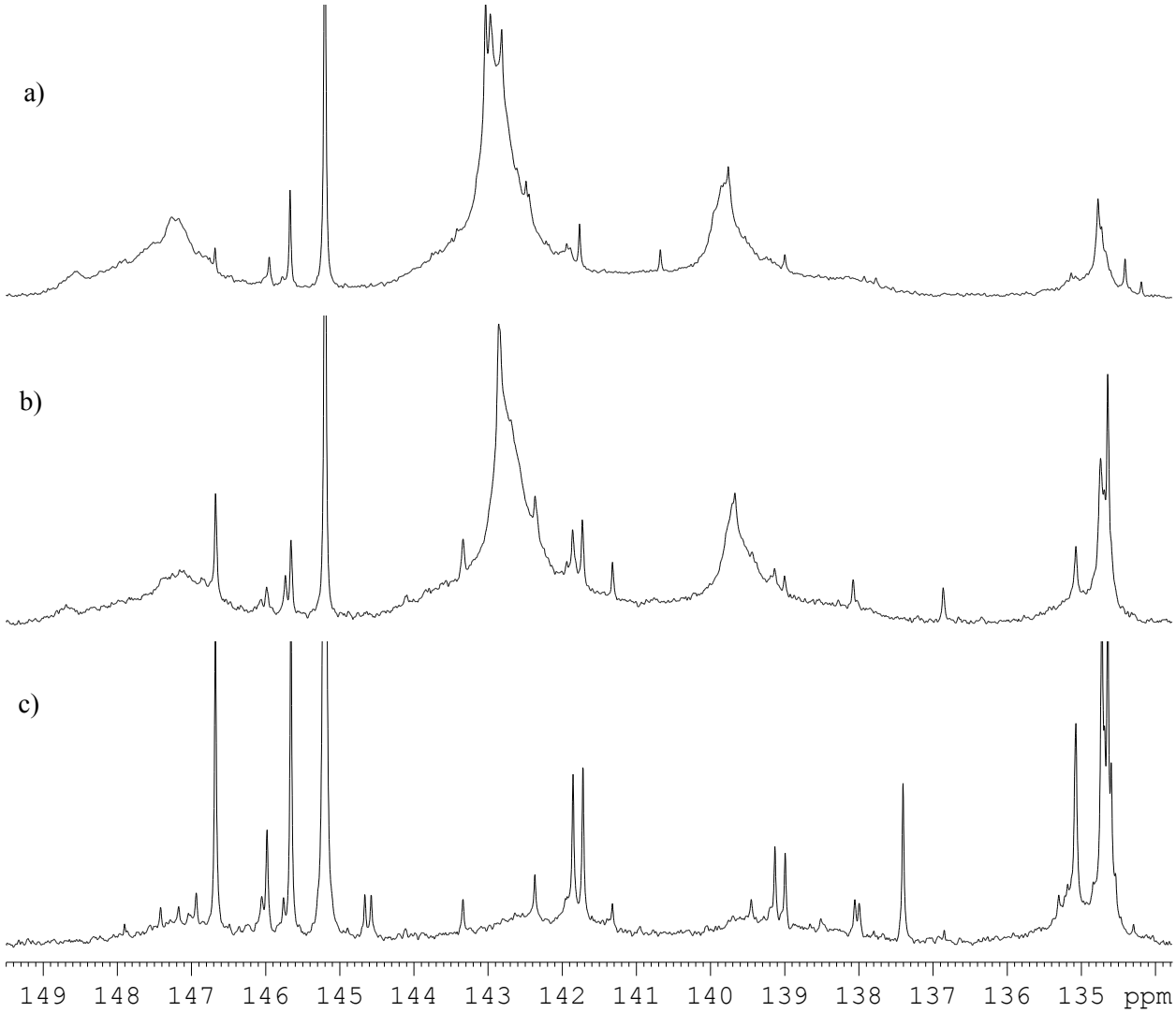

Figure S31. Quantitative $^{31}P\{^{1}H\}$ NMR spectra (121 MHz, line broadening 2.5 Hz) of derived phosphite esters from a) organosolv lignin, b) control experiment (base with no catalyst) and c) residue after the catalytic lignin oxidation using 10 wt. % **2** and 10 wt. % Et_3N. For all runs: solvent = EtOAc; temperature = 100 ^{o}C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.